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Rapid determination of iodine-129 in large-volume water samples using rotary evaporation preconcentration and accelerator mass spectrometry measurement

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Abstract

A rapid method using rotary evaporation combined with accelerator mass spectrometry (AMS) measurement, was developed for the determination of ^{129}I in large-volume water samples. The parameters including water bath temperature, pH, concentration volume and reducing reagent, were thoroughly optimized. The chemical yield of iodine under the

optimal conditions is between 98.8 and 100.7%. Compared to the direct evaporation, the enrichment time can be shortened by five times. The measured $^{129}I/^{127}I$ ratios for the environmental water samples are in good agreement with those previously reported values, suggesting this method is accurate, roubust and suitable for ^{129}I determination in large water samples.

Keywords

^{129}I, Large-volume, Water samples, Rotary evaporation, Accelerator mass spectrometry

Introduction

Iodine has only one stable isotope, ^{127}I and the only long-lived radionuclide is ^{129}I (half-life of 15.7 Ma) [1]. ^{129}I is naturally generated via cosmic ray reactions with xenon in the upper atmosphere, spontaneous fission of ^{238}U and thermal neutron-induced fission of ^{235}U in the earth (with a total inventory of 250 kg in the environment).

The sources of ^{129}I in the environment are currently dominated by human activities, with a total inventory of approximately 6100 kg released mainly by reprocessing of nuclear fuel as of 2009 [2, 3]. The anthropogenic ^{129}I has dispersed to large area, $^{129}I/^{127}I$ ratios in the environment have increased by 1 to 6 orders of magnitude compared to the level in the pre-nuclear age [4-6]. The conservative behavior in oceans and the physicochemical properties of iodine, as well as the long half-life, make ^{129}I ideal for many applications, such as tracing the movement and exchange of water masses in the seas [7, 8], tracing the atmospheric behavior and process of iodine [9], providing

knowledge on geochemical cycling of stable iodine [10, 11], tracing the migration of organic matter and age dating of marine geological events between 2 and 80 Ma [12-15].

Natural ^{129}I is ideal as a hydrologic tracer owing to being soluble and highly mobile in any hydrologic environment [16]. Fabryka-Martin et al. [16] have presented ^{129}I data in ground water samples collected from the Great Artesian Basin, Australia. Along with other hydrogeological evidence, this work suggests large-scale mixing of waters between Cretaceous and Jurassic formations, intrusion of atmospheric iodine to the groundwater and in-situ production of ^{129}I from an underlying formation significantly higher in uranium content. Despite this high potential, applications of ^{129}I in hydrogeological system have so far been limited, because it generally needs large-volume water samples. At least 1 mg of stable iodine (^{127}I) is required for a measurement, but the environment concentration of ^{127}I is very low, for example, only 1-10 μg/L of iodine are present in meteoric, surface and ground water [17]. A large amount of sample is also needed for the analysis of pre-nuclear samples. For instance, the analysis of a freshwater sample with ^{127}I concentration of 5 μg/L, and an $^{129}I/^{127}I$ ratio of 10^{-12}, requires at least 10 L sample to obtain a reliable measurement results. Thus, pre-concentration of iodine from water samples is necessary. The methods are mainly anion exchange chromatography, direct evaporation by heating and rotary evaporation. Anion exchange chromatography is relatively complicated, time-consuming with more than 12h for 10 L water sample, and suffer from low iodine recovery of about 50-87% [18]. Direct evaporation at sub-boiling conditions is conventionally used, giving a high iodine recovery (>90%) but also taking a long time. For instance, it takes more than 20 h to concentrate a water sample from 5 L to 1 L [19, 20]. Rotary evaporation method is operated under pressure for continuous

distillation of volatile solvents, with the advantage of being fast and efficient. This method has been used for freshwater samples from the orange county aquifer system, California, and 40 rivers of the USA, Canada and Western Europe [21-23]. However, it is not clear so far whether the rotary evaporation process cause iodine a loss, and to what extent it will influence the chemical yield of iodine.

This work aims to investigate the influence and corresponding mechanisms of the various rotary evaporation parameters on the recovery rate of iodine, and to obtain optimal operation conditions for rapid determination of ^{129}I in large-volume water samples. Finally, the optimized experimental conditions were applied to the determination of ^{129}I in several environmental water samples.

Experimental

Samples, chemicals and instruments

Four water samples were analyzed in this study. Two rainfall samples were collected on the roof of the Xi'an Accelerator Mass Spectrometry Center (34°13′25.23″N, 108°59′58.89″E) on 8th December, 2015, and stored in PE containers in dark until analysis. A lake water sample was collected from a public garden in the center of Xi'an (34°15′17″N,108°58′38″E) on 2nd September, 2017, and stored in an airtight polyethylene container. An underground water sample was collected in Hancheng of Shaanxi province (35°28′45.9″N, 110°23′41.1″E), and stored in dark until analysis.

All chemical reagents used in this work are of analytical grade, mainly including $NaHSO_3$, HNO_3, $NaNO_2$, $AgNO_3$, $K_2S_2O_8$ and NaOH purchased from Sinopharm Chemical Reagent Co., Ltd (China). Iodine carrier with an $^{129}I/^{127}I$ atomic ratio of 2×10^{-14}

was obtained from Woodward Company (USA). ^{129}I standard solution (NIST-SRM-4949C from the National Institute of Standard and Technology, Gaithersburg, MD, USA) was used to prepare ^{129}I standards for the AMS measurement. Na^{125}I solution (Chengdu Gaotong isotope corporation, China) was used as a tracer. Niobium powders (325 mesh, 99.9%) was purchased from Alfa Aesar Company (Ward Hill, MA, USA). All solutions were prepared using deionized water of 18.2 MΩ/cm, produced by Cascada TM Lab Water System (Pall Life Sciences, USA).

The rotary evaporation system consists of a rotary evaporator (RE-52AA, Shanghai Yarong Biochemical Instrument Factory, China), a circulating vacuum pump (SHB, Zhengzhou Great Wall science and technology co. Ltd) and a low-temperature coolant circulation pump (DLSB-5/20, Zhengzhou great wall science and technology co. Ltd). A gamma counter (Model FJ2021, Xi'an Nuclear Instrument Factory, China) was for ^{125}I decay counting for the calculation of the chemical yield. A 3 MV Tandetron AMS (HEVV, The Netherlands) at the Xi'an AMS Center was employed to determine ^{129}I. An inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8800, USA) was used to measure stable ^{127}I.

Iodine enrichment using rotary evaporation

In a first experiment 1L deionized water was transferred to a rotary evaporator. 500 Bq of ^{125}I was added, and then deionized water was preconcentrated by rotary vacuum distillation. In this work, the concentration process was optimized by investigating the effect of various parameters, including water bath temperature (50-80 °C), pH of sample solution (7-13), reductant concentration (0-10 mmol/L) and final concentration volume

(10-120 mL). After concentration, 1 mL of water samples was taken to count ^{125}I for calculating the chemical yield of iodine. Three replicates were done for each experiment.

Separation of iodine from samples

Water samples were filtered through a 0.45μm membrane to remove the suspended particulate matter. 1 mL of the filtered sample was taken for the determination of total iodine (^{127}I). Large-volume water samples (1-5 L) were preconcentrated by the rotary evaporation system. After iodine enrichment, $K_2S_2O_8$ was added to a final concentration of 30 g/L. The sample was then incubated at 60°C for 20 h to decompose organic substances, and for converting organic iodine into inorganic form [24]. The samples were transferred to a separation funnel for solvent extraction. 1 mg of iodine carrier, 200 Bq of ^{125}I tracer and 2-3 mL of 1 mol/L $NaHSO_3$ were added. After thoroughly mixing, 3.0 mol/L HNO_3 was added to adjust the pH to 1 to 2, and 15 mL of CCl_4 was added, and 2-4 mL of 1 mol/L $NaNO_2$ solution to oxidize iodide to I_2. The formed molecular iodine (I_2) was then extracted into the CCl_4 phase by shaking. After transferring CCl_4 from the funnel to a beaker, a second 10-15 mL of new CCl_4 was added to the funnel to extract the remaining iodine. The CCl_4 phases were combined and transferred to a new separation funnel. 10 mL of H_2O and 0.5-1.0 mL of 0.1 mol/L $NaHSO_3$ solution were added for back extraction of iodine. The extraction and back-extraction process was repeated once more. After removal of the CCl_4 phase, the water phase was transferred to a 15 mL centrifuge tube. ^{125}I in the separated solution in the centrifuge tube was counted using the gamma detector, and the recovery of iodine in the separation procedure was calculated by comparing the ^{125}I count in the samples to those in a ^{125}I standard solution with the same volume. After ^{125}I measurement, 1.0 mL of 1.0 mol/L $AgNO_3$ was added to the separation

solution in the centrifuge tube to precipitate iodide as AgI. The separation AgI was washed using deionized water, and the separated AgI was dried at 60℃ for 2-3 h. After ground to fine powder, 3 times (by weight) niobium powder was weight and mixed with the AgI powder, the mixture was pressed into a copper holder for the AMS measurement of $^{129}I/^{127}I$ ratio.

Determination of ^{129}I and ^{127}I

$^{129}I/^{127}I$ atomic ratios in the prepared targets were measured by AMS using the 3MV tandem AMS system (HVEE) at the Xi'an AMS center. I^- ions sputtered from the ion source were accelerated and passed through a stripper to strip off several electrons of iodine. I^{5+} was chosen for the measurement, consequently $^{127}I^{5+}$ was measured as charges (current) using a Faraday cup and $^{129}I^{5+}$ was measured using a gas ionization detector. The sample was measured for 6 cycles, and each sample for 5 min in each cycle.

Total iodine (^{127}I) concentrations in water samples were measured by ICP-MS using an Agilent 8800 ICP-MS (Thermal Electron Corporation), under hot plasma conditions (RF of 1500 W), with the Xt interface. 10 mL filtered water was diluted by an appropriate factor using 0.5% Tetramethylammonium hydroxide (TMAH) solution, and $^{133}Cs^+$ (CsCl) was spiked as internal standard to a concentration of 2.0 ng/mL.

Results and discussion

Effect of water bath temperature on recovery and evaporation time

Water bath temperature is one of the parameters to determine distillation speed, which was investigated from 50°C to 80°C by using deionized water with addition of ^{125}I tracer.

The results show that chemical yield of iodine increases with temperature increasing from 50°C to 60°C, and then decreases from 60°C to 80°C, with a peak value of 95.3±1.43% at 60°C (Fig. 1). The chemical reaction rate of iodide oxidation in aqueous solution is affected by the temperature [25]. The oxidation rate will increase with increasing temperature. Therefore, the lower recovery of iodine at higher temperature might be attributed to the formation of volatile iodine species (e.g. HIO, I_2) [26, 27]. In contrast, a relatively lower recovery was observed at 50°C, which might be attributed to long evaporation time [28], approximately two times longer as that at 60°C (Fig. 1). The evaporation time to concentrate from 1 L to 100 mL is greatly reduced from 155.0±3.0 min at 50°C to 58.5±1.5 min at 80°C. For 60°C, with optimal recovery of iodine, about 73.5±1.1 min is necessary. Base on both evaporation time and iodine recovery, 60℃ is selected as the optimal water bath temperature.

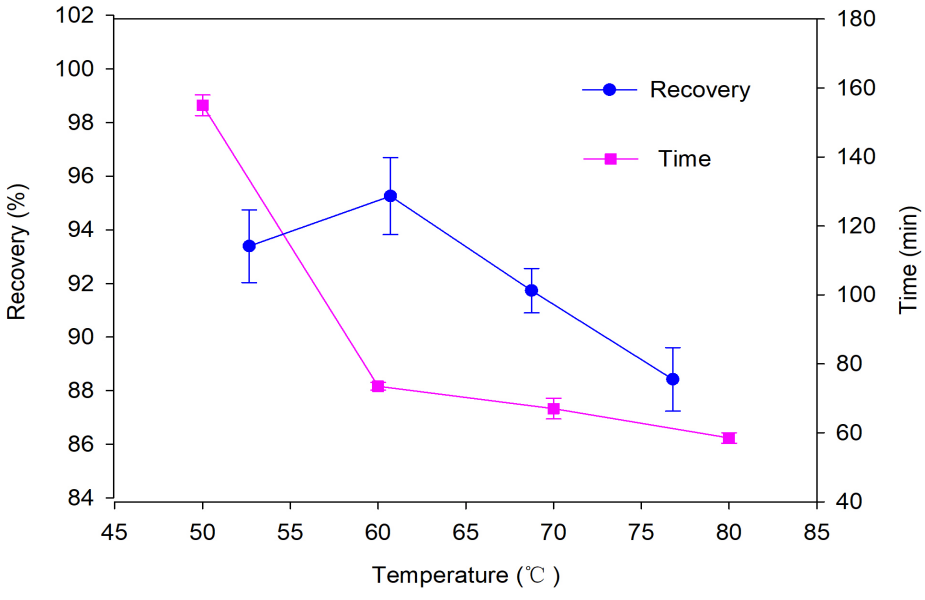


Fig.1 Effect of water bath temperature on iodine recovery and evaporation time.(The sample is deionized water with addition of ^{125}I; Initial water volume, 1 L; Final concentrated volume, 100 mL).

Effect of pH on recovery of iodine

Even with the optimal water bath temperature (60℃), there is still a 5% loss of iodine, which might be attributed to the pH of sample solution and formation of volatile iodine species. The experiment above was conducted using a neutral solution. Iodide is more stable under alkaline conditions [29], thus, the effect of solution pH is investigated by adjusting from 7 to 13.

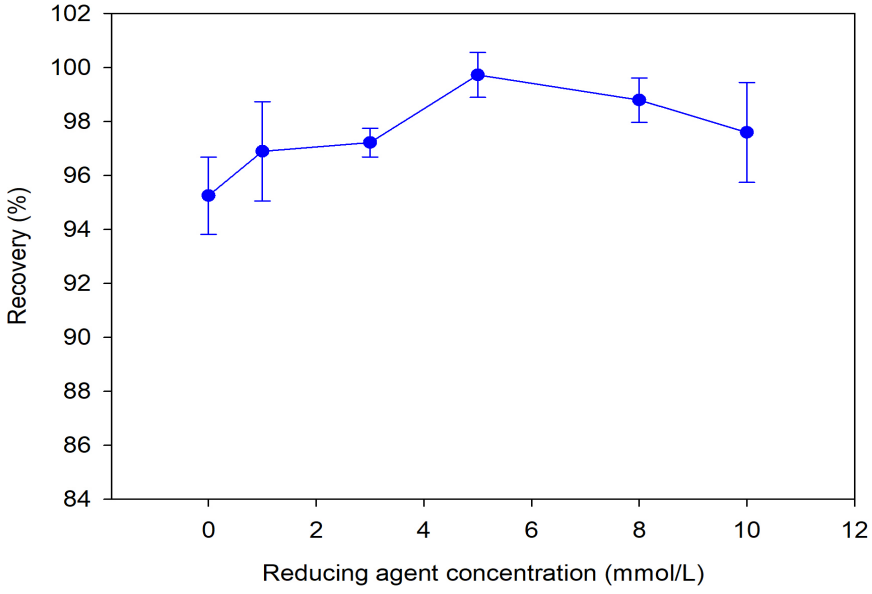
The results show recovery of iodine in the range of 94-95% and no significant change was found (Table 1). Increase in pH and decrease in the redox potential could reduce the formation of volatile iodine [30-33]. However, in alkaline solution, the electrode potential of O_2 is higher than the electrode potential of I^-, so iodine redox reaction can still occur (Eq.(1))[3, 33]. Since the experiment was carried out under vacuum, volatile iodine species escape more easily, and the chemical reaction was push to the right of the equation. Therefore, pH 7 was selected as the optimal pH value.

$$2\,I^- + 1/2O_2 + H_2O \longleftrightarrow I_2 + 2OH^- \qquad (1)$$

Effect of reductant concentration on recovery of iodine

Alternatively, addition of a reducing agent may inhibit iodine loss caused by formation of volatile species. The effects of $NaHSO_3$ addition on the recovery of iodine were investigated in a water bath at 60℃and pH=7. The reductant concentrations in the sample solution were set at 1 mmol/L, 3 mmol/L, 5 mmol/L, 10 mmol/L. As shown in Fig.2, with

187 the increase of reducing agent from 0 to 5 mM, the recovery of iodine increased from
188 95.3±1.4% to 99.5±0.8%, followed by a slightly decrease when the reducing agent
189 concentration was more than 5 mmol/L. The results suggest that addition of reductant
190 could effectively inhibit the oxidation of I^- to HIO/I_2 and avoid iodine loss. During the
191 experiment, it was observed that when the reductant concentration increases, a large
192 amount of bubbles appear during distillation. Therefore, it can be speculated that the
193 decrease in recovery might be attributed to decomposition of $NaHSO_3$ to produce SO_2
194 gas, which promotes the reaction of I^- in the solution with O_2 in the distillation flask and
195 thus reduces the recovery of iodine.



196

197 **Fig.2** Effect of reductant concentration on iodine recovery. (Sample: deionized water;
198 Water bath temperature, 60°C; Initial water volume, 1 L; Final concentrated volume, 100
199 mL; pH =7).

200 **Effect of final concentrated volume on iodine recovery**

The water was concentrated to a final volume of 120 mL, 100 mL, 50 mL, 20 mL and 10 mL at a water bath temperature of 60℃, pH of 7 and a $NaHSO_3$ concentration of 5 mmol/L. As shown in Table 1, when the volume was concentrated from 120 mL to 100 mL, there is basically no iodine loss (99.7 ± 1.3% and 99.5±0.8%). When the final concentrated volume was reduced from 100 mL to 10 mL, iodine recovery gradually decreased. This is because the time required for concentrating the water sample to a smaller volume gradually increases. In a same water bath temperature, the longer the time, the lower the efficiency of iodine recovery [28]. In summary, 100 ml is selected as the optimal final concentrated volume.

Table 1 Effect of pH (Group 1) and concentrated volume (Group 2) on iodine recovery*

Group 1				**Group 2**		
pH	**Initial volume (mL)**	**Concentrated volume (mL)**	**Recovery (%)**	**Concentrated volume (mL)**	**Initial volume (mL)**	**Recovery (%)**
7	1000	100	95.3±1.4	10	1000	95.2±0.5
8	1000	100	94.4±0.8	20	1000	95.6±1.4
11	1000	100	94.0±0.6	50	1000	97.3±1.1
13	1000	100	95.3±1.3	100	1000	99.5±0.8
				120	1000	99.7±1.3

* Group 1: Effect of pH on iodine recovery. (Sample: Deionized water; Water bath temperature, 60°C; pH adjustment is performed by NaOH); Group 2: Effect of concentrated volume on iodine recovery (Sample: Deionized water; Water bath temperature, 60°C; pH=7; Reductant concentration, 5mmol/L).

215

216 With the optimal experimental conditions obtained above, environmental fresh water
217 samples were analyze for ^{129}I, including rain, lake and ground water samples.
218 The chemical yields of iodine among these samples are shown in Table 2. At the
219 same initial volume (1 L), a slightly lower recovery of iodine of 93.3-95.5% was
220 observed for the real environmental water samples in comparison to deionized water
221 (99.5±0.8 %). This difference might be caused by the presence of organic matter in rain
222 and lake water. The content of dissolved organic matter in rainwater was reported to be
223 0.33-31.58 mg/L [34]. In the process of rotary evaporation, the organic matter in the
224 water sample reacts with the reducing agent to consume a part of the reducing agent,
225 weakened the reducing effect of the reducing agent on I_2, so that the actual iodine
226 recovery of the water sample is lower than that of the deionized water. For ground water,
227 a recovery of 89.0 ± 2.4 % was achieved for a 5 L sample. The 5 L water was equally
228 divided into five aliquots. The first 1 L water was preconcentrated to a volume of 200
229 mL, and then added another 1 L water sample until the total of 5 L water was finally
230 concentrated to 100 mL. For each 1 L water sample, the recovery of iodine can be
231 calculated to be 97.7% by extracting the quintic root, which is comparable with the
232 recovery for deionized water. This also confirms the influence of organic matter in real
233 water samples. In addition, rain water samples were subjected to experiments comparing
234 recovery with and without addition of reducing agent. The recoveries are 95.4±0.4% and
235 93.3±1.3% in the presence and absence of reductant, respectively. The result shows that
236 the addition of reducing agent slightly improves the recovery of iodine in real water
237 samples. Iodine in less than 1 L rainwater samples can be directly separated and purified

by solvent extraction [3, 35, 36]. However, for samples over 1 L, the low phase volume ratio in the extraction process results in recovery of less than 85%, and is highly organic solvent–consuming, time-consuming and labor-intensive. In this case, the sample is firstly concentrated and then subjected to solvent extraction or direct precipitation. The advantage is obvious: small sample size, easy to operate, shortened time, less organic solvent used and high recovery of iodine (>90%).

As shown in Table 2, the traditional heating plate evaporation method takes more than 20 hours to concentrate 5L water samples to 1L, rotary evaporation only 5 hours from 5 L to 0.1 L, indicating that the rotary evaporation method can greatly reduce sample preparation time at least 4 times.

The analytical results of $^{129}I/^{127}I$ atomic ratios in two rainwater, one lake water and one ground water samples are shown in Table 2. The $^{129}I/^{127}I$ ratios are (23.5±2.4) $\times10^{-10}$ and (24.5±2.5) $\times10^{-10}$ for rain water samples with and without addition of reductant, respectively, (5.67±0.28) $\times10^{-10}$ for lake water, and (0.1±0.05) $\times10^{-10}$ for ground water. These results are in good agreement with those published in our previous work [19, 20, 37], indicating that the rotary evaporation method is accurate, time saving and suitable for ^{129}I analysis of large-volume environmental water samples.

Table 2 Analytical performance and results of $^{129}I/^{127}I$ atomic ratios in environmental water samples.

Sample	Sampling location	Methods*	Initial Volume (mL)	Final concentrated volume (mL)	Time (h)	Recovery (%)	$^{129}I/^{127}I$ ($\times10^{-10}$) this work	$^{129}I/^{127}I$ ($\times10^{-10}$) in Refs.

Rain	Xi'an	1	1000	100	1.2	95.4±0.4	23.5±2.4	24.6±2.1[37]
Rain	Xi'an	1	1000	100	1.2	93.3±1.3	24.5±2.5	24.6±2.1[37]
Lake water	Xi'an	1	1000	100	1.2	93.4±1.5	5.68±0.28	5.74±0.32
Ground water	Hancheng	1	5000	100	5	89.0±2.4	0.10±0.05	0.11±0.04[20]
Rain	Xi'an	2	700-1500	100-300	10-12	91.7-99.5	-	-[19]
Ground water	Hancheng	2	5000	1000	> 20	92.0-99.9	-	-[20]

* Methods: 1. Rotary evaporation followed with solvent extraction;

2. Direct evaporation method using a hot plate below 100 °C.

Conclusion

In this study, the experimental conditions of water bath temperature, water sample pH and reductant addition are optimized in detail. The results show that when pH is 7, concentration of reducing agent is 5 mmol/L, water bath temperature is 60 ℃, and final concentrated volume is 100 mL, the iodine recovery is as high as 99% for deionized water and slightly lower (> 93%) for real environmental water samples. This study also suggests that improper conditions of rotary evaporation will cause iodine loss of 5% or even up to 15%, which will underestimate ^{129}I concentration in environmental water samples. Compared with the traditional low-temperature evaporation method, the rotary evaporation method can effectively shorten the iodine pre-enrichment time by at least four times. Therefore, the rotary evaporation method is feasible and suitable for ^{129}I

analysis in large-volume environmental water samples, and this can serve to broaden ^{129}I tracing applications in hydrogeological systems. Furthermore, this method can also be used for reserving large-volume water samples in a smaller sample size.

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